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BOROHYDRIDE CATALYSIS OF NITRAMINE
THERMAL DECOMPOSITION AND COMBUSTION:
III. LITERATURE REVIEW AND WRAP-UP DISCUSSION
OF POSSIBLE CHEMICAL MECHANISMS

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This report is a summary of observations and possible chemical mechanisms for catalysis of the decomposition and combustion of the nitramines HMX and RDX, and of propellants derived from them, by salts containing the anions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$. Available literature data on the thermal behavior of salts containing these anions is reviewed, as is available information on the effects of these salts on decomposition and combustion of HMX and RDX. The emphasis is on thermal decomposition and on salts with alkali metal anions. The pure salts appear stable under vacuum or inert gas to about 700-800°C, but there is a report of H_2 evolution at about 620-650°C. In the presence of air, thermooxidative degradation at somewhat lower temperatures (ca 300-600°C, depending on the nature of the salt) is observed. When the salts are heated together with RDX, considerable enhancement of the decomposition rate of RDX is observed; this begins at the melting temperature of pure RDX and becomes intense, leading to a lower, much sharper decomposition exotherm. These observations seem consistent with a catalysis mechanism involving attack of the B-H hydrogens of the catalyst on the nitramine, but it is difficult to evaluate the role of other processes, and of reaction of the catalyst with products.			
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I. INTRODUCTION

There are a number of applications, such as the monolithic charge and the traveling charge, for which very high burning rate (VHBR) propellants are needed. These propellants generally contain HMX or RDX and/or triamino-guanidinium nitrate (TGN), together with a borohydride such as one of the HIGHLIGHTS (Teledyne-McCormick-Selph). The borohydride, which is often a $B_nH_n^=$ salt such as $K_2B_{10}H_{10}$ or $K_2B_{12}H_{12}$, greatly accelerates the burning rate of the propellant. This effect is quite well-known, and has been the subject of several workshops and of a large number of reports.^{1,2,3,4}

The purpose of the present work is to elucidate the chemical mechanisms responsible for the burning rate acceleration of HMX and RDX propellants by $B_nH_n^=$ salts, with the ultimate goal of optimizing propellant formulations for actual use, i.e., maximum "catalytic" effects with minimum sensitivity. This work has been focussed on the initial stages of the nitramine decomposition process; however it should be remembered that it is possible that catalysis may also occur at a later stage of the combustion process, when the initial products such as H_2CO , NO_2 , N_2O , HCN , etc., are reacting with each other.

Previous reports in this series^{5,6} have described pyrolysis-GCMS studies on RDX and on RDX- $K_2B_{12}H_{12}$ mixtures,⁵ and on a series of HMX-TGN propellant compositions,⁶ some uncatalyzed and some catalyzed with $K_2B_{10}H_{10}$. Reference 5 is considered to be Part I of this series, and Reference 6 to be Part II.

The present report is a summary and critical analysis of data in the literature on borohydride catalysis of the initial stages of nitramine decomposition, together with a discussion of some possible chemical mechanisms that may be involved.

II. EFFECT OF ADDED $K_2B_{10}H_{10}$ AND $K_2B_{12}H_{12}$ ON THERMAL DECOMPOSITION OF THE NITRAMINES HMX AND RDX

In this section we will consider the effect⁵⁻¹³ of added $K_2B_{10}H_{10}^=$ and $K_2B_{12}H_{12}^=$ salts on the rates and product distributions of the nitramines HMX and RDX. The decomposition of mixtures⁵⁻¹³ of pure salts and of the pure nitramines will be considered separately.

A. Effect of Added Catalyst on Decomposition Rates

There are few if any quantitative kinetic studies of the decomposition of HMX and RDX in the presence of $B_{10}H_{10}^=$ and $B_{12}H_{12}^=$ salts; however there is some qualitative information in support of the view that addition of the above salts does accelerate the early stages of thermal decomposition of these materials.

First, thermal analysis studies have been performed¹³ on mixtures of RDX with $K_2B_{12}H_{12}$, with $((CH_3)_4N)_2B_{12}H_{12}$ and with $NaBH_4$; these show that the normal RDX exotherm at ca 240°C is shifted to the noticeably lower temperature of ca 200°C, and appears to coincide with the normal RDX melting endotherm at this temperature. The mixtures used contained 15-50% of the boron compound.

This same effect is also observed¹³ when RDX is mixed with $((\text{CH}_3)_4\text{N})_2\text{B}_{12}\text{H}_{12}$ that has been heat treated at 480°C; but the acceleration effect is almost eliminated when the heat-treatment takes place at 760°C. It also seems worth mentioning that little if any acceleration is observed when elemental boron is substituted for the above salts.¹³

The above DSC studies¹³ employed open pan- (no lids) with argon purge flow of 30 ml/min. It was pointed out that there was thus little chance for gas to collect over the sample; the above effects were thus believed due to solid/liquid phase interactions.

Second, a series of experiments was reported^{10,11} in which RDX, alone and in mixtures containing 29% $\text{K}_2\text{B}_{12}\text{H}_{12}$, was partially decomposed at temperatures of 200-215°C. The residues from the incomplete decomposition of these samples were analyzed by HPLC; it was found that addition of $\text{K}_2\text{B}_{12}\text{H}_{12}$ led to more rapid disappearance of RDX and appearance of its mononitroso derivative (MRDX). This indicates that $\text{K}_2\text{B}_{12}\text{H}_{12}$ accelerates decomposition of RDX, in agreement with the DSC results described in the preceding paragraphs.

B. Effect of Added Catalyst on Product Distributions

Gaseous-Product Catalyst Effects. There is little quantitative information available on the effect of added B_nH_n^- salts on gaseous-product distributions. It was found from pyroprobe-GC studies^{9,11} that the relative amounts of HCN, NO, and NO_2 were greater for RDX decomposed in the presence of borohydride catalysts than for RDX decomposed alone. Tantalum hydride and tantalum oxide did not affect the decomposition products to the same degree as the borohydride catalysts. Pyroprobe-GC-FTIR studies¹³ indicated that the main effect of added borohydride catalyst was an increase in CO_2 formation relative to N_2O .

Catalyst Effects on Formation of Less-Volatile Products. A number of less-volatile products have been identified as being formed from the decomposition of HMX and RDX.^{5,6,13,14,15,16} These include 1,3,5-triazine;^{5,6} 1,3,5-triazine N-oxide;^{5,6} a material(s?) with parent peak at m/e = 97 (protonated form, m/e = 98),^{14,16} usually written as 1,3,5-triazine C-oxide; formamide;^{5,13} N-methylformamide;^{14,16} N,N-dimethylformamide;^{14,16} dimethylnitrosoamine;^{14,16} dimethylamino-acetonitrile;^{6,14} an unidentified compound,⁶ hereinafter referred to as Unknown A (1,2,4-oxadiazole?) with its parent peak at m/e = 70; and a number of unknown compounds.^{5,13}

The effect of added $\text{K}_2\text{B}_{10}\text{H}_{10}^-$ and $\text{K}_2\text{B}_{12}\text{H}_{12}^-$ on formation of 1,3,5-triazine and its N-oxide seems to be to reduce the relative extent to which they are formed.^{5,6} These catalysts also reduce formation of the 1,3,5-triazine oxide (C-oxide?) detected by Snyder, Kremer and Reutter,¹⁵ at least relative to dimethylformamide, dimethylacetonitrile and dimethylnitrosoamine.

On the other hand, added $\text{K}_2\text{B}_{10}\text{H}_{10}^-$ and $\text{K}_2\text{B}_{12}\text{H}_{12}^-$ lead to an increase in the relative amounts of dimethylaminoacetonitrile,⁶ N-methylformamide, N,N-dimethylformamide and dimethylnitrosoamine formed.¹³

Unknown A exhibits an interesting dependence on addition of catalyst;⁶ at low temperatures added $\text{K}_2\text{B}_{12}\text{H}_{12}^-$ leads to a decrease in its formation from RDX

decomposition, while at higher temperatures an apparent increase in its formation is observed on addition of $K_2B_{12}H_{12}^-$.

III. THERMAL BEHAVIOR OF PURE SALTS OF THE ANIONS $B_{10}H_{10}^-$ AND $B_{12}H_{12}^-$

In understanding the mechanisms by which the anions $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ catalyze the decomposition and combustion of HMX and RDX, it is necessary to understand the thermal behavior of these materials separately. In the present section, the thermal behavior of salts of $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ will be summarized; the emphasis will be on thermally-stable, non reducible cations such as metals since this will eliminate complications due to decomposition reactions involving the anions. In the following section the behavior of HMX and RDX will be summarized.

It has been reported¹⁷ that when metal (or other not-readily-reduced cation) salts such as $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ were heated under vacuum in sealed tubes to temperatures of 600-800°C, they were recovered unchanged except for melting. Since cesium and potassium are both alkali metals, the potassium salts $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ that are of interest as propellant combustion catalysts may well behave similarly.

Kuznetsov and Klimchuk¹⁸ have described the preparation, infrared spectra and thermal properties of the $B_{12}H_{12}^-$ salts of sodium, rubidium, cesium, lithium and hydronium. The thermal studies were mainly of the thermo-gravimetric and DTA types, and were carried out under air. It was found that the thermooxidative degradation of all of the compounds began with a distinct exothermic effect at about 300°C, with the stability increasing appreciably from the lithium to the cesium salt. This thermooxidative degradation was accompanied by an increase in weight of the compounds; the increase in weight was linked by infrared studies to replacement of B-H bonds by B-O bonds. However no definite composition could be assigned to these pyrolysis products.

Note that in the studies described in Reference 18, thermooxidative degradation of these materials was observed, while in Reference 17 it was stated that the materials were unchanged; this discrepancy is probably due to the fact that the studies of Reference 18 were carried out under air, while those of Reference 17 were carried out in a sealed tube. This seems relevant to the question of the behavior of these materials in the presence of nitro compounds such as HMX and RDX, since such materials would also be expected to provide an oxidizing environment.

In a study¹⁹ of sodium closo-dodecaborate tetrahydrate, it was found that the material gave two endotherms at 140°C and 195°C; these were connected with the two-stage elimination of water (two molecules at each stage). The anhydrous salt existed in the region 195-505°C, and above 505°C this was found to undergo exothermic thermooxidative degradation marked by an increase in weight corresponding to one oxygen atom per formal unit of the anhydrous salt. This mono-oxygenated product burned on being heated above 830°C. Presumably the heating was carried out under air, in view of the occurrence of oxidative processes.

Another Russian paper²⁰ described thermogravimetric and DTA studies on a series of mixed potassium, rubidium and cesium dodecahydro-closo-dodecaborate halides. The salts investigated had the composition $M_2B_{12}H_{12} \cdot MX$, where M was

K, Rb or Cs and X was Cl, Br or I. The thermoanalytical studies were performed under air at a heating rate of 9 K per minute, and it was found that the thermooxidative degradation of the mixed salts began in the range 510-570°C, regardless of the nature of the cation and the halogen. This degradation was accompanied by an increase in weight; this increase was attributed to replacement of the B-H bond by B-O and to a gradual conversion of the tetrahydroborate ion into alkali metal borates and B_2O_3 .

The thermal decomposition of the hydrogen analogs $H_2B_{12}X_{12} \cdot nH_2O$, where X is H, Cl, Br or I and n is 4-12, has been investigated²¹ by mass spectrometry and IR spectroscopy in the temperature range 20-800°C. When $H_2B_{12}H_{12} \cdot 6H_2O$ was heated to 400°C, evolution of water and hydrogen was observed. Above 400°C, boron ions (B^+) were seen for all compounds investigated. The $B_{12}Cl_{12}^-$ and $B_{12}Br_{12}^-$ ions also showed BX^+ , BX_2^+ and BX_3^+ . It was argued that the B^+ ions resulted from ionization of elementary boron, since their temperature dependence had the same form as that of elementary boron.

In the course of studies on a variety of boron hydride derivatives, thermal analysis studies were performed on some $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ salts.²² The cesium salts of $B_{12}H_{12}^-$ gave only two exothermic effects with "insignificant" gassing at 616-655°C. It was stated that nearly one mole of H_2 was given off per mole of salt in this temperature range; however the identification of H_2 as the gas was not described. The infrared spectrum for $Cs_2B_{12}H_{12}$ after heating to 700°C retained all primary absorption bands of the untreated salt. Curves were also given for $Cs_2B_{10}H_{10}$ which suggested that this compound behaves similarly. If substantiated, this report of H_2 evolution suggests that slight changes involving H_2 evolution may also have taken place in the sealed-tube vacuum heatings described in Reference 17, and quite possibly in all such experiments on these compounds. The studies described above were in vacuum. The effect of medium was noted only for the cesium and tetramethylammonium $B_{12}H_{12}^-$ salts. When the experiments were carried out in argon, behavior was similar to that in vacuum and when it was carried out in air, exothermal thermooxidative behavior was observed at 200-300°C, accompanied by an increase in weight.

Thermolysis studies on $((CH_3)_4N)_2B_{12}H_{12}$ were also described;²² the situation is complicated by the presence of the tetramethylamino group. The authors felt that the decomposition involved destruction of the tetramethylamino cation and possibly formation of a B-N bond. Thermal studies on $(NH_3)_2B_{10}H_{12}$ and $(NH_4)_2B_{10}H_{10}$ are also described.

Duff and Decker¹³ described a variety of thermoanalytical studies on $K_2B_{12}H_{12}$ and on $((CH_3)_4N)_2B_{12}H_{12}$. These studies were performed in an atmosphere of argon. It was found that the potassium salt gave a weak endotherm at 78°C, corresponding to about 7 percent weight loss, and was thereafter stable to at least 460°C. The tetramethylammonium salt, on the other hand, remained stable until a temperature of about 360°C was reached, at which temperature it exhibited an endotherm and an 18.5 percent weight loss. The catalytic ability of these salts toward RDX decomposition was not decreased by preheating at 360°C.

It is tempting to try to explain the above weight losses¹³ in terms of loss of water molecules from stable hydrates. Note the above description¹⁹ of a similar phenomenon involving sodium dodecaborohydride. This would be in

agreement with the following: (a) The 7 percent weight loss of the potassium salt corresponds approximately to that expected for loss of one molecule of water from a hydrate, and the 18.5 percent weight loss for the tetramethylamino compound corresponds approximately to loss of four molecules of water from a hydrate; (b) these weight losses do not remove the catalytic effect of the salt on RDX decomposition. However the water-loss hypothesis does not explain the slight discoloration noted.¹³

Several other publications^{23,24} appear to contain information on thermal properties of $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ salts, but it has not yet been possible to obtain these papers in English translation.

On the basis of the above, it is possible to draw several conclusions about the thermal behavior of the pure $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ salts. First, in the absence of air they seem stable to temperatures well above the initial decomposition temperatures of HMX and RDX. Second, at elevated temperatures they seem to undergo oxidation reactions with the oxygen of air; it does not seem unreasonable to suppose that analogous behavior might occur in the presence of other oxidizing atmospheres such as might be provided by nitrogen oxides, or by the nitro groups in liquefied HMX or RDX.

IV. THERMAL DECOMPOSITION BEHAVIOR OF PURE HMX AND RDX

The thermal decomposition chemistry of pure HMX and RDX, together with some possible chemical mechanisms, have been reviewed previously.²⁵⁻²⁸ The present report will therefore be concerned only with updating these reviews with regard to new results in those areas that seem most relevant to the question of mechanisms of borohydride catalysis. These include (a) identification of a number of products involving reduction, as well as reassignment of the structures assigned to some very common ion masses (such as m/e 46, 74, 75) that have been previously observed in mass spectrometric studies of HMX and RDX decomposition; and (b) some very interesting results on Infrared Multiphoton Dissociation.

A. Products Involving Reduction

Probably the one recent development most pertinent to the question of catalysis of HMX and RDX decomposition by $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ is the detection¹³⁻¹⁶ of products, such as formamide, N-methylformamide, N,N-dimethylformamide, dimethylaminoacetonitrile, etc., from decomposition of pure HMX and RDX.

Some of these products have probably been detected in previous mass spectrometric studies on HMX and RDX decomposition, but misidentified because their molecular weights are similar to those of materials which are, or at least might logically be expected to be, products of HMX or RDX decomposition. Typical examples of such products include formamide (detected¹⁴ as its protonated form, m/e 46) (same as NO_2); dimethylformamide (detected¹⁴ as its protonated form with m/e 74) (same as $H_2C=N-NO_2$); dimethylnitrosamine (detected as its unprotonated (m/e 74, same as $H_2C=N-NO_2$) or protonated (m/e 75, same as protonated $H_2C=N-NO_2$)) forms.

We have already alluded above to the effects of added $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ on formation of these products.

Initially, formic acid, formamide, N-methylformamide, N,N-dimethyl-formamide and dimethylnitrosamine were detected by GC-FTIR studies¹³ on HMX and RDX decomposition. Also detected were several unidentified compounds, which were believed to contain C-nitroso, C=N double-bonded, ketone and amide groupings.

The use of pyrolysis together with Atmospheric Pressure Chemical Ionization Mass Spectrometry (APCI-MS) led to the detection, from RDX decomposition, of principal nongaseous products with molecular ions of m/e 46, 60, 74, 75, 85, 98.^{14,15} Surprising results emerged from examination of the daughter-ion mass spectra of the decomposition products from isotopically-labeled and unlabeled HMX and RDX. Use of deuterium and ¹⁵N-labeled samples of RDX allowed deduction of the molecular formulas of these species; m/e 46 proved to be not NO₂ but protonated formamide; m/e 60 proved to be protonated N-methylformamide; m/e 74 proved to be not H₂C=N-NO₂ but protonated N,N-dimethylformamide; and m/e 75 proved to be not protonated H₂C=N-NO₂, but protonated N,N-dimethylnitrosamine. The products with m/e 85 and 98 proved to be the protonated forms of dimethylaminoacetonitrile and of a 1,3,5-triazine oxide respectively. (The protonation is believed to have taken place inside the mass spectrometer, the original products being the unprotonated forms.) The effects of added K₂B₁₀H₁₀⁺ and K₂B₁₂H₁₂⁺ salts were also studied; these were described earlier in the present report.

Many of these same products were also detected from studies¹⁶ in which small solid samples of HMX and RDX were heated in an alumina reaction cell and product concentrations during pyrolysis were studied by allowing small amounts of products to escape through an orifice into a low-pressure chamber and studying the electron ionization (EI) mass spectra of the products. Time-of-flight velocity spectra were used to determine the molecular weight of the products contributing to each ion-mass signal arriving at the detector; in this way it was possible to eliminate the ion-fragmentation peaks and concentrate on the actual products of thermal decomposition. Both gaseous and nongaseous products were studied. Although the EIMS technique did not permit structures to be determined as in the triple quadrupole CI study,¹⁴ the use of deuterated and ¹⁵N-labeled samples gave formulas consistent with the structures measured under APCI conditions.¹⁴

Some possible chemical mechanisms for formation of these reduced, hydrogenated products are discussed in Section C. below.

B. Infrared Multiphoton Decomposition

Another very interesting recent piece of work on RDX decomposition is the infrared multiphoton dissociation molecular-beam study by Zhao, Hintsa, and Lee.³¹ In this work, a molecular beam of RDX molecules was crossed by a pulsed CO₂ infrared laser beam; vibrational excitation by this beam was used to simulate thermal excitation. The products were analyzed by mass spectrometry. Products having m/e 120, 119, 102, 80-82, 74, 56, 46, 44, 42, 26-30, and 12-17 were observed. No signal was detected between m/e 120 and 222 (RDX molecular ion). Velocity distributions were used to help identify the sources of these products. The results were interpreted in terms of two simultaneous mechanisms for the gas-phase decomposition of RDX: (a) synchronous, one-step decomposition of RDX into three molecules of H₂C=N-NO₂

(m/e 74); and (b) N-NO_2 cleavage followed by stripping of HNO_2 to give 1,3,5-triazine (m/e 81). $\text{H}_2\text{C=N-NO}_2$ was considered to decompose by two channels, one leading to formation of H_2CO and N_2O and the other leading to formation of HCN and HNO_2 .

However there are a number of factors which should be understood better before applying these gas-phase results and mechanisms uncritically to decomposition in the condensed phase. These include the question of, to what temperature does the type and degree of vibrational excitation provided by the infrared laser excitation employed³¹ correspond? The decomposition of HMX and RDX produces predominantly N_2O and H_2CO at lower temperatures and predominantly species such as NO_2 , HCN, etc., at higher temperatures. The relative amounts of products such as HCN, NO_2 , and HONO given³¹ seems to be much larger than relative amounts of products such as N_2O and H_2CO , suggesting that the results apply to a high temperature process. Thus the question of the applicability of these results to decomposition at lower temperatures deserves further investigation.

Another question involves the possible role of excitation and deexcitation by intermolecular collisions in condensed-phase decomposition. When vibrational excitation takes place stepwise by these collisions rather than in one step, will the RDX molecules go to a point where they decompose to give three $\text{H}_2\text{C=N-NO}_2$ from one step, or will they undergo stepwise decomposition or "unzipping" before reaching this point? Furthermore, will the molecules which reach highly-excited vibrational states decompose by concerted cleavage or will stepwise decomposition become more important?

It also seems worth mentioning that although as pointed out above, the detection of products other than $\text{H}_2\text{C=N-NO}_2$ with masses of 74 and 75 suggests that many earlier attributions of m/e 74 and 75 to unprotonated and protonated $\text{H}_2\text{C=N-NO}_2$ may have been in error, the mass 74 peak described by Zhao, Hintsza and Lee³¹ is probably in fact due to $\text{H}_2\text{C=N-NO}_2$. This follows from the high-vacuum conditions used, and from the fact that the temperatures attained by the unreacted RDX (130°C and 154°C) seem low enough to preclude thermal decomposition prior to vibrational excitation by the laser beam. However for complete rigor, isotope studies might be helpful here.

C. Chemical Mechanisms for Decomposition of the Pure Nitramines HMX and RDX

Overall Decomposition Mechanisms. Possible chemical mechanisms for decomposition of pure HMX and RDX have been discussed previously.²⁸⁻³⁰ The details are still about as uncertain as they were at the time of the earlier discussion; the main change seems to be that the concerted decomposition pathway (concerted depolymerization to three (RDX) or four (HMX) molecules of $\text{H}_2\text{C=N-NO}_2$), which was mentioned previously,²⁸ has had its credibility greatly enhanced by the infrared multiphoton decomposition (IRMPD) results of Zhao, Hintsza, and Lee.³¹

The paper of Zhao, Hintsza, and Lee³¹ includes results suggesting that RDX decomposition proceeds primarily by concerted depolymerization to 3 $\text{H}_2\text{C=N-NO}_2$ which decompose to either N_2O and formaldehyde, or by HONO elimination to HCN and HONO. However this result corresponds to a thermal decomposition at a very high temperature (ca 1000°C); there is at least one piece of evidence which suggests that at a lower temperature either (a) stepwise decomposition

of RDX involving initial N-NO_2 cleavage, followed by breakup of the resulting nitrogen-centered radical to $\text{H}_2\text{CN}^\bullet$ and two molecules of $\text{H}_2\text{C=N-NO}_2$ or (b) N-NO_2 cleavage of $\text{H}_2\text{C=N-NO}_2$ may take place. This is the detection³² by ESR, of the radical $\text{H}_2\text{CN}^\bullet$, the formation of which seems hard to explain²⁸ except by one of the above mechanisms.

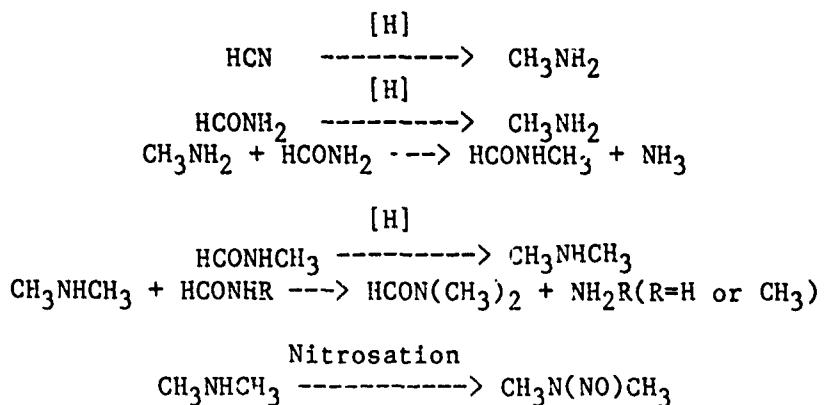
Thus, it seems quite possible that stepwise ring cleavage and loss of two molecules of $\text{H}_2\text{C=N-NO}_2$ from the nitrogen-centered denitro-RDX radical, and/or N-NO_2 cleavage of $\text{H}_2\text{C=N-NO}_2$ to give $\text{H}_2\text{CN}^\bullet$ and NO_2 could be taking place at the lower temperature ranges (200-300°C) in which the decomposition of HMX and RDX is being studied.

Formation of Reduced and Hydrogenated Species. Because of their possible importance to mechanisms of borohydride catalysis, it seems appropriate to discuss possible mechanisms for formation of the hydrogenated materials (Formamide (HCONH_2), N-methylformamide (HCONHCH_3), N,N-dimethylformamide ($\text{HCON}(\text{CH}_3)_2$), dimethylnitrosamine ($\text{CH}_3\text{N}(\text{NO})\text{CH}_3$), and dimethylaminoacetonitrile ($(\text{CH}_3)_2\text{NCH}_2\text{CN}$) from pure HMX and RDX.

It is known²⁸ that H_2 is formed in decomposition of HMX and RDX. The mechanisms for its formation are uncertain, but presumably they involve either dimerization of H^\bullet or reaction of some source of H^\bullet (for example $\text{H}_2\text{CN}^\bullet$ or HCO^\bullet) with another H-source molecule or with H^\bullet . Since their large hydrogen content suggests that the formamide derivatives, dimethylaminoacetonitrile, etc., are the product of reduction/hydrogenation reactions, it seems reasonable to suspect that they share a common source with, or possibly are formed from, the H_2 .

A possible source for formamide might be partial hydrolysis of HCN which is known²⁸ to be formed, along with water required for its hydrolysis, from HMX/RDX decomposition.

It is difficult to predict just how HCN, formamide and related compounds might react under the exact conditions present in molten HMX/RDX at temperatures in the range ca 200 - 800 degrees. However it is known³³ that catalytic hydrogenation, or reduction with many common reducing agents, of nitriles and amides generally leads to the corresponding amines. Therefore it seems logical that HCN or formamide could conceivably be reduced to methylamine, CH_3NH_2 , by the hydrogen atoms or precursor present.



SCHEME I

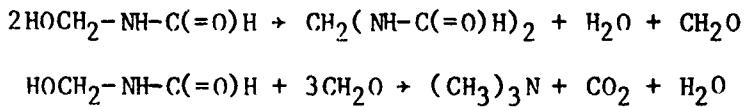
Methylamine formed in one of these ways could then react with formamide to give N-methylformamide, which could be reduced to dimethylamine; this could then react, by nucleophilic displacement at the carbonyl group, with formamide or N-methylformamide to give dimethylformamide. Nitrosation of dimethylamine, by nitrogen oxides (NO and NO₂) known²⁷ to be formed in HMX and RDX decomposition, could lead to dimethylnitrosoamine.

Formation of (CH₃)₂NCH₂CN and related compounds could be explained by dimerization or oligomerization of H₂CN[•], which is known to be formed in thermal decomposition of HMX and RDX.³² Tail-to-tail dimerization of H₂CN[•] followed by rearrangement of hydrogen atoms could lead to H₂NCH₂CN, which could react with formamide to yield HCONHCH₂CN; this could then hydrogenate at the carbonyl yielding CH₃NHCH₂CN. The above process could then be repeated adding another methyl group and ending up as (CH₃)₂NCH₂CN. Another pathway might begin with dimerization of cyanide radical to give cyanogen (NC-CN), which might react with (CH₃)₂NH followed by hydrolysis and/or hydrogenation to give (CH₃)₂NCH₂CN.

A large number of possible pathways to these hydrogenated products (formamide and its methylated derivatives, dimethylnitrosamine and (CH₃)₂NCH₂CN) can be written; the possibilities are limited primarily by how many reaction pathways for nitriles and carbonyl groups are remembered from elementary organic chemistry. The main feature of the above is probably the source of the reduction; it presumably arises from the hydrogen atom source(s) which also give rise to the H₂ formed in HMX and RDX decomposition.

If they occur, these apparent H-atom hydrogenation pathways would be mechanistically significant, since their occurrence suggests that the H-atoms should also be available for autocatalysis^{28,29} by attack on the nitro oxygens of HMX and RDX.

Another redox reaction that may be involved in the formation of the hydrogenated products is suggested by the work of Cosgrove and Owen,³⁴ who reported formation of an amine nitrate from RDX decomposition in a static system just below its melting point at 195°C. They were unable to identify the amine, but suggested it might have been trimethylamine, which they suggested could have been formed from decomposition of hydroxymethylformamide (a known decomposition product of HMX and RDX) with formaldehyde, via the following mechanisms:



SCHEME II

It is then possible that reduction of CH₂(NH-C(=O)H)₂ and/or 2HOCH₂-NH-C(=O)H might lead, possibly via CH₂(NH-CH₃)₂ or HOCH₂-NH-C(=O)H respectively, to dimethylamine ((CH₃)₂NH). Furthermore, oxidation of trimethylamine ((CH₃)₃N) might lead to such compounds as dimethylformamide.

V. SOME POSSIBLE CHEMICAL MECHANISMS FOR CATALYSIS OF HMX AND RDX DECOMPOSITION BY $B_{10}H_{10}^-$ AND $B_{12}H_{12}^-$

In this section we will discuss some possible chemical mechanisms which may be responsible for catalysis of HMX and RDX decomposition and combustion by boron-containing salts such as $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$.

A striking manifestation of the rate-enhancing effect of these salts on HMX and RDX decomposition is provided by the DSC curves of the catalyzed and uncatalyzed nitramines.¹³ The melting endotherm of RDX at ca 205°C and its broad, intense decomposition exotherm at ca 225-250°C disappear and are replaced by a sharp, exothermic spike in the region 203-224°C; this spike is so narrow and intense that it appears to have no width at all. Examination of these curves¹³ suggests that the rate enhancement occurs immediately on melting of the RDX, since for the catalyzed samples the melting endotherm disappears and the reaction becomes rapid at precisely the temperature (ca 205°C) at which uncatalyzed RDX melts. Since these studies were done in open pans,¹³ which enabled the gaseous products such as nitrogen oxides to escape, it was suggested that direct nitramine-catalyst interactions occurred. However, some gas-catalyst interactions could still occur under these confined conditions. The object of the following discussion will be to explain this large decomposition-rate enhancement.

It is possible to conceive of at least three general classes of initial steps which might contribute to catalysis of HMX and RDX decomposition by borohydride salts such as $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$:

1. Decomposition of nitramine is initiated by direct reaction between nitramine and borohydride; for example, as discussed below, by electron transfer, by attack of a B-H hydrogen on nitro oxygen of the nitramine or by some combination of these mechanisms.
2. An early decomposition product of the nitramine, for example NO_2 , reacts with the catalyst to form products, possibly free radicals, which react further with the nitramine, resulting in catalysis.
3. Unimolecular decomposition of the catalyst generates products or radicals which react with nitramine, causing it to decompose faster than would otherwise be the case.

At least at low temperatures, Class 3 seems less likely than the others, in view of the reports^{13,17,22} that when heated in vacuum or in an inert atmosphere, alkali metal salts of $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ are stable up to temperatures in the range of 600-800°C. The available data offer support for both Class 1 and Class 2. The intense nature of the above rate enhancement, its correlation with increased contact due to melting of the RDX, and the open-pan nature of the studies suggests that 1 may be the more likely. Note however that RDX and HMX decompose below their melting points and that the decomposition accelerates on melting.²⁷ Therefore it seems premature to conclusively rule out explanation 2, especially with regard to gaseous, strongly oxidizing products such as NO_2 .

Possible types of chemical mechanisms that might be operating include the following:

A. Attack of a B-H hydrogen of the catalyst on the HMX or RDX molecule, most likely at the oxygen of the nitro group.

B. An electron-transfer reaction between the catalyst and the nitramine molecule, with the nitramine assuming a negative charge and the boron-containing anion assuming one less negative charge than before.

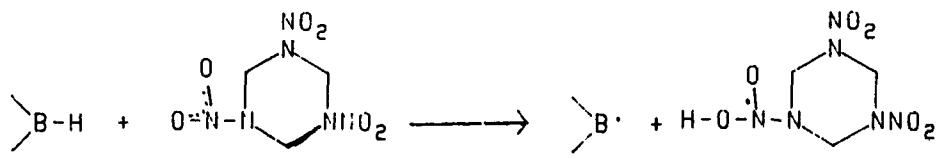
C. Primary decomposition of the nitramine, followed by reaction of one or more of the products (most likely NO_2 , although other products, especially other nitrogen oxides such as NO and N_2O are also plausible candidates) with the catalyst, generating more radicals or other intermediates which catalyze the decomposition further.

D. Another possibility might be an equilibrium involving the boron-containing salt in which a B-H bond breaks thermally to give a hydrogen atom and a boron-centered radical; hydrogen atoms formed in this way could dimerize to H_2 . The hydrogen atoms could also react with nitramine, presumably at the oxygen atom of the nitro group, and the resulting hydroxynitroxide could decompose to give OH^\cdot and nitrosoamine; or to give HONO and nitrogen-centered denitro-RDX radical.

Mechanisms A and B are examples of Class 1, mechanism C is an example of Class 2, while mechanism D is an example of Class 3, and accordingly seems less likely except at higher temperatures.

A number of the observations in the preceding sections are consistent with the idea that the subject catalysis may involve hydrogen-atom donation by the borohydride ($\text{B}_{10}\text{H}_{10}^-$ and $\text{B}_{12}\text{H}_{12}^-$) anions. These include the following: (a) (Section IIB) the relative amount of reduced products (formamide derivatives, etc.) tends to increase on addition of catalyst.^{13,15} (b) It was reported²² (Section III) that heating of $\text{Cs}_2\text{B}_{10}\text{H}_{10}$ and $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ in vacuum led to evolution of almost 1 mole of H_2 per mole of salt, accompanied by a slight endotherm in the region around 600-650°C. Examination of the gas-evolution curves shows that while evolution is fastest in the 600-650°C region, there is for both compounds a long tail to the low-temperature side of the volume-time plot. This remains visible down to just above 400°C, and there may conceivably be a very small amount at even lower temperatures. In any case, the high-temperature evolution of hydrogen gas (H_2) suggests the possibility that even at low temperatures the B-H bonds might be sufficiently labile as to be susceptible to attack, possibly by nitro oxygens on the nitramine. (c) In connection with (b) it seems worthwhile to mention the observations¹³ that when $((\text{CH}_3)_4\text{N})_2\text{B}_{12}\text{H}_{12}$ was heat-treated at 460°C it retained its catalytic activity toward RDX decomposition, but lost it when the heat-treatment took place at 760°C. Elemental boron had no catalytic activity.

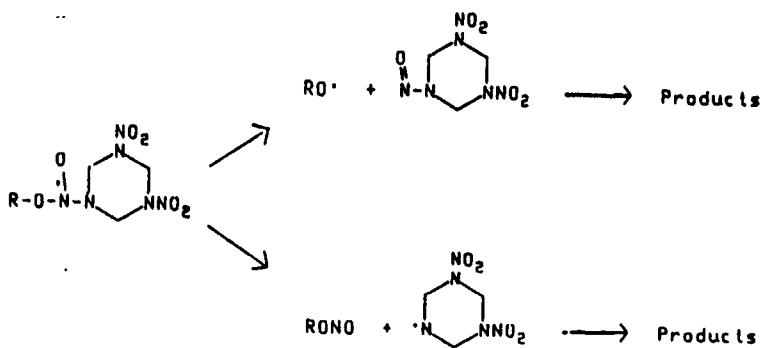
One possible mechanistic scheme for the initial phases of catalysis might be as follows:



where a nitro group of RDX reacts with a B-H bond of the anion of the catalyst salt ($B_{10}H_{10}$ or $B_{12}H_{12}$).



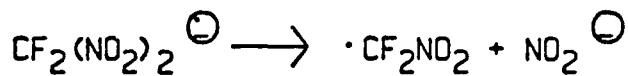
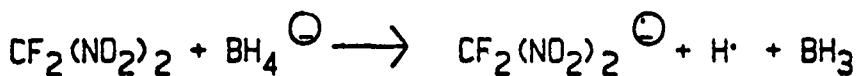
SCHEME IV



SCHEME V

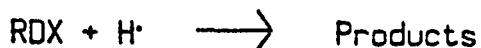
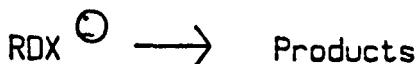
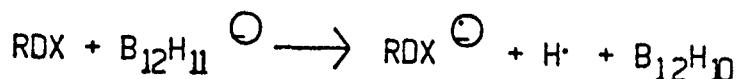
In Scheme V, $R = H\cdot$ or $B\cdot$. Note however that the exact details in the above schemes are uncertain. In particular, there is at present not enough information to evaluate the importance, if any, of electron transfer reactions.

A variation on the theme of electron transfer reactions might be a combination of electron-transfer and hydrogen-transfer mechanisms; such a combination has been suggested in the Russian literature³⁵ for reaction of difluorodinitromethane with a variety of nucleophilic reagents, including sodium borohydride. The radicals produced were studied by ESR and trapping techniques, and identified as $H\cdot$ and $\cdot CF_2NO_2$. Their formation was rationalized in terms of the following mechanism:



SCHEME VI

An analogous mechanism for catalysis of HMX/RDX decomposition by $B_{10}H_{10}^-$ or $B_{12}H_{12}^-$ could be written as follows:



SCHEME VII

VI. RELATIONSHIP TO COMBUSTION OF VHBR PROPELLANTS

We now attempt to show how the above may relate to the combustion of VHBR propellants. The burning of a series of VHBR propellants has been studied and photographed in a transparent chamber.³⁶ The first phase of combustion was a relatively slow porous burning that proceeded through the sample, leaving behind a porous residue that retained the form and about 90% of the weight of the original sample. There was then a transition to very rapid combustion throughout the entire sample, accompanied by some deconsolidation.

Since the propellants contained about 10% of boron compound (referred to as "fuel", the figure of 90% of the original weight remaining after the first phase makes sense if some of the boron hydride remained solid after the first phase, and absorbed some of the oxygen from the $-NO_2$ groups on the nitramine. The weight lost presumably was due to gaseous products of HMX/RDX or TAGN decomposition.

It is possible to imagine this first phase of combustion as beginning through either of two processes: (a) Nitramine melts and on contact of liquid nitramine with solid boron hydride, decomposition begins, possibly by the bimolecular H-transfer process. This leads to increased heating which causes more nitramine to melt; nitramine melting is driven through the sample by the heating until the entire sample has reacted in this way, with each molecule of boron hydride promoting decomposition of approximately one mole of nitramine. At this point, the sample is porous and surrounded by nitramine-decomposition gases. Combustion and heat release then begin in earnest in the gas phase, possibly catalyzed further by boron compounds in either the gas or solid phases. (b) Nitramine begins to decompose and an early decomposition product, poss'ibly NO_2 , reacts with boron hydride causing catalysis of nitramine decomposition as described above. Each molecule of boron hydride causes decomposition of approximately one mole of nitramine, and finally the sample is porous and is surrounded by nitramine-decomposition gases.

Combustion and heat release then begin in earnest in the gas phase, possibly catalyzed further by boron compounds in either the gas or solid phases.

VII. SUGGESTIONS FOR FUTURE WORK

On the basis of the above discussion, it is possible to make a number of suggestions for future work that might be helpful in understanding the catalytic action on nitramine decomposition of salts containin, the anions $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$.

First, note that much of the above discussion is based on studies on lithium, sodium, cesium and rubidium salts of the anions $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$. It would be useful to have some of studies repeated on the potassium and tetramethylammonium salts that actually seem to be of primary interest as catalysts.

Quantitative kinetic studies on catalysis by these salts are also needed. Another type of study that would be of interest is H-D isotope effect studies. Comparison between salts of $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ on the one hand, and their deuterated analogs $B_{10}D_{10}^-$ and $B_{12}D_{12}^-$ on the other, could yield valuable information on the role of the B-H bonds in catalysis. Careful control of particle size of both nitramine and catalyst would probably be necessary, in order to obtain results with quantitative significance.

Further information on reactions of these salts with nitrogen oxides such as NO_2 , NO , and N_2 would also be helpful in evaluating the catalytic role of reaction between catalyst salts and product gases.

Another type of study that would be useful would be studies of the effect on ^{15}N scrambling between un- and fully (all nitrogens, both nitro and amino) labeled HMX and RDX, of $B_{10}H_{10}^-$ and $B_{12}H_{12}^-$ salts. These studies would be useful in detecting any mechanism shifts involving $N-NO_2$ cleavage equilibria.

Finally, identification of the species referred to in the section entitled, "Catalyst Effects on Formation of Less-Volatile Products" as "Unknown A" (Is this 1,2,4-oxadiazole?). An understanding of the structure and formation mechanisms of this material seems especially interesting in view of the possibility that the temperature-variation in the catalyst effect on its formation may be related in some way to the apparent evolution of H_2 from $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ in the temperature range of ca 600-650°C.²²

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